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RATES OF INTRAMOLECULAR CONVERSIONS OVER LOW BARRIERS
(U) CORNELL UNIV ITHACA NY DEPT OF CHEMISTRY
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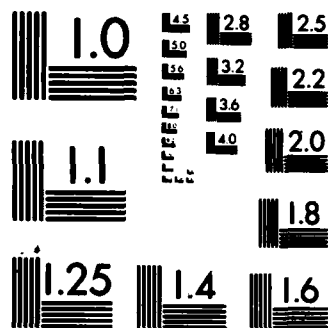
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FINAL REPORT

RATES OF INTRAMOLECULAR CONVERSIONS
OVER LOW BARRIERS

AFOSR-80-0046

CORNELL UNIVERSITY
DEPARTMENT OF CHEMISTRY
ITHACA, NEW YORK 14853

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FINAL REPORT

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INTRAMOLECULAR UNSYMMETRICAL OHO BONDS. THERMOCHEMISTRY

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Most O---H-O bonds are unsymmetrical; this report deals with nearly symmetric potential wells, slightly perturbed by the next to nearest neighbor environment. The ratios of residence times of the hydrogen atom in the two-well potentials in unsymmetrically substituted acetylacetones were derived from NMR chemical shifts at the carbonyl carbons (^{13}C natural abundance), recorded for dilute solutions of the enol isomers in nonpolar solvents. Cross-checks between several equilibrium constants indicate that the motion of the bridging hydrogen atom is strongly coupled to (indeed, is largely determined by) the dynamics of the molecular skeleton.

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Chief, Technical Information Division

Reprinted from The Journal of Physical Chemistry, 1983, 87, 2411.

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SECOND ORDER RATE CONSTANTS FOR INTRAMOLECULAR CONVERSIONS:

APPLICATION TO GAS-PHASE NMR RELAXATION TIMES;

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The usually quoted expression for the second order rate constant, for a unimolecular reaction at the low pressure limit, is valid only for strictly irreversible processes. Its application to isomerization reactions (which are to some extent reversible) is demonstrably in error; corrected expressions have been published. Attention is directed to intramolecular conversions over low barriers, for which the inappropriateness of the unidirectional expression becomes obvious. For such isomerizations we propose a model which incorporates only operationally observable states, so that an essential conceptual ambiguity is avoided. Use of this model is illustrated for the $\text{syn} \rightleftharpoons \text{anti}$ conversions of methyl nitrite, derived from a gas phase NMR coalescence curve ($M_c:T_c$). The present data suggest that during isomerization the alkyl nitrites may not be completely ergodic on a time scale of 10^{-9} s. A regional phase-space model is proposed which has the appropriate formalism to account for this behavior.

Reprinted from The Journal of Chemical Physics, 79, 2808 (1983).

INTRAMOLECULAR CONVERSION RATES OVER LOW BARRIERS II.

THE ALKYL NITRITES

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Relaxation times for intramolecular conversions in alkyl nitrites (syn \rightleftharpoons anti) were measured via dynamic NMR spectroscopy, both in CDCl_3 solutions and in the gas phase. The pressure range covered was (120-4.0 Torr), at corresponding temperatures (293-205) $^\circ\text{K}$. Equilibrium constants were checked, and rates were estimated both from coalescence points ($M_C; T_C$) and broadened lineshapes. A consistent assignment of chemical shifts is presented. The preponderance of data, from several sources, lead to a barrier of approximately 10 kcal mole $^{-1}$ for these interconversions. The magnitudes of bimolecular rate constants deduced for samples at the higher densities are in agreement with values calculated from appropriately corrected RRKM equations, but rate constants found for low density samples were considerably larger than those predicted. A regional phase-space model is proposed which accounts for this discrepancy. It is based on the postulate that when the density of states is low ($\approx 40/\text{cm}^{-1}$ for H_3CONO at the barrier summit) nanoseconds are required for full redistribution of energy over all vibrational phase space.

Will appear in August, Journal of Physical Chemistry.

INTERMOLECULAR CONVERSION OVER A LOW BARRIER, III.

Gas-Phase NMR Studies of an H-Bond Association

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Measurements of gas phase NMR spectra of mixtures of $(\text{CH}_3)_2\text{O}$ and HCl , for mole ratios (1:1+1:4), at total pressures 400-40 Torr, over the temperature range 300-212°K, led only to a lower bound for k_{uni} , in the limiting low pressure regime. These data confirm the published values for $\Delta H^\circ_{\text{ass}} = -6.9$ kcal/mole and $\Delta S^\circ_{\text{ass}} = 25.6$ e.u. Two of the low wagging frequencies proposed for the adduct had to be raised from 50 to 100 cm^{-1} to obtain agreement between the calculated and observed $\Delta S^\circ_{\text{ass}}$. From the NMR spectra it was possible to derive estimates of equilibrium vapor pressures of $(\text{H}_3\text{C})\text{O}:\text{HCl}$, and of its heat of vaporization. The activation energy for dissociation of the adduct cannot be greater than 8.5 kcal/mole.

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Submitted to Journal of the American Chemical Society.

CONVERSIONS OVER LOW BARRIERS IV.
STUDIES OF FORMIC, ACETIC AND THIOFORMIC ACIDS, and

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Nuclear magnetic resonance spectra were recorded of gaseous formic and thioformic acids, from room temperature down to 211°K, for pressures 15±2.5 Torr. The monomer-dimer equilibrium was monitored for HCOOH, and the trans-cis conversion in HCOSH. These data indicate that the relaxation time for the former is consistent with an RRKM rate calculated in the second-order regime for an $E^0 \approx 12$ kcal mole⁻¹. The latter process is considerably more rapid than the expected isomerization relaxation rate, predicted from the rotational barrier height about the C-S bond, derived from microwave spectra.

Temperature dependent NMR spectra were also obtained of dilute solutions of the three acids in CDCl₃ and CD₂Cl₂. A line-width analysis of the acetic acid spectra indicate the presence of an excited state of the dimer which has not been previously proposed.

Submitted to Journal of the American Chemical Society.

CONVERSIONS OVER LOW BARRIERS. V.

The Acetyl-Acetones (Gas Phase).

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(LONG ABSTRACT -- of manuscript in preparation)

We chose to investigate various rates at which acetylacetones interconvert in the gas phase. These are the classical examples of enol-keto tautomerism, wherein the enol form is stabilized by intramolecular H-bonding. Since a number of conformers are present it is necessary to refer to Fig. 1. Here we indicated the estimated relative ground state energies for the combination $Y = CH_3$ and $X = CF_3$. Depending on the nature of X and Y, at room temperature and a pressure of about 10 torr, 85-99% of the gas is in the enol form. The slowest conversion occurs over an estimated barrier of 20 kcal/mole.

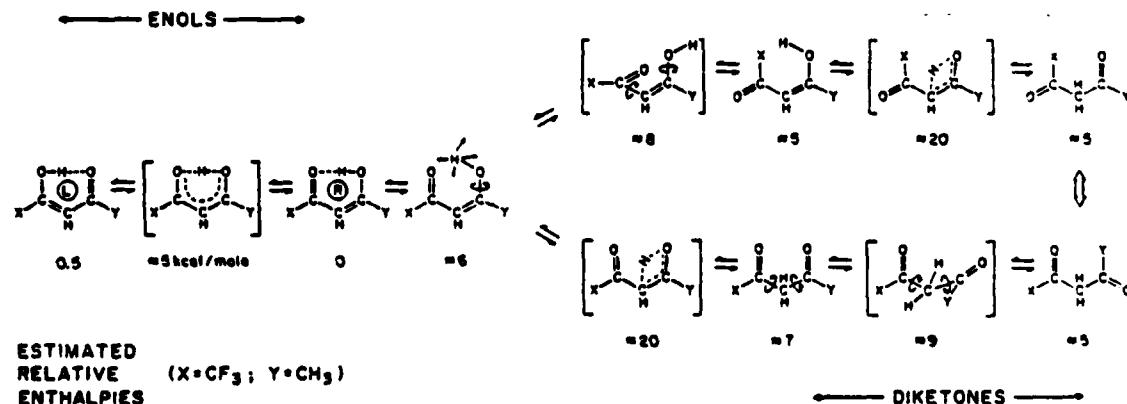


Figure 1. Significant molecular configurations by the acetylacetones, with postulated transition structures.

In the T-jump method, mixtures of acetylacetone (10 to 50 Torr), SF_6 (≈ 1 Torr), with and without added argon, were rapidly heated by ≈ 1 ms pulses of CO_2 laser radiation. Changes in the infrared spectrum were recorded via a weak monitoring beam normal to the laser beam (see Fig. 2).

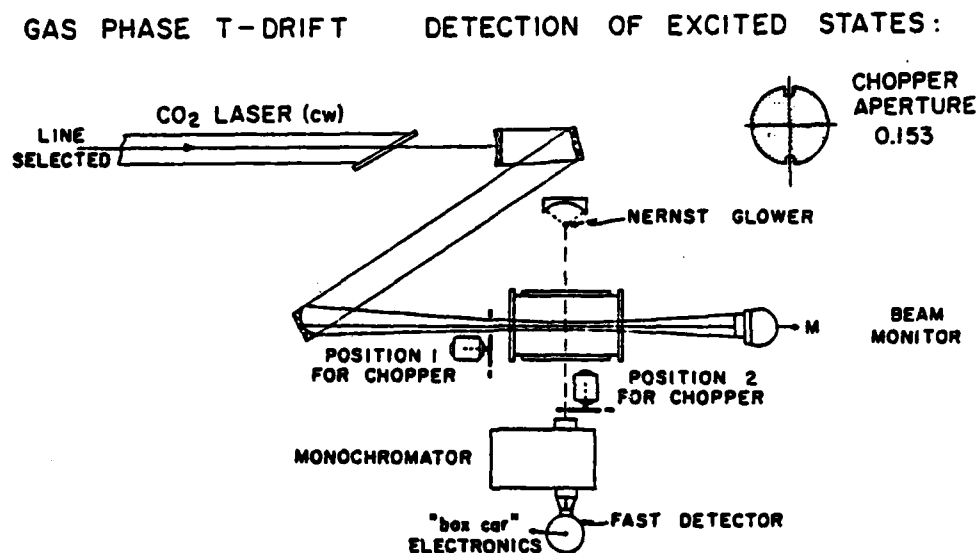


Figure 2. Schematic of the experimental configuration for pulse heating the core of the sample cell.

We noted decrements in the assigned bands (in the vicinity of $1550\text{--}1750\text{ cm}^{-1}$), and the appearance of new transient features which we ascribe to the diketo forms. [At present we cannot distinguish between them.] The time dependence of the rise and decay of the transient spectral features, their pressure and temperature dependence give us the desired rate parameters.

The optimum ir bands for monitoring the $\text{enol} \rightleftharpoons \text{keto}$ conversion are associated with the $\text{C}=\text{O}$ stretch vibration, which on ketonolization shift to higher frequencies. The absorption due to the hydrogen bond is too weak to be useful. Ogoshi and Nakamoto [JCP (1966) 45, 3113] presented a complete normal mode

analysis and band assignment for the enol isomer of the acetyl-acetones, but found no bands which could be assigned specifically to the keto form (due to the low concentration of the latter).

In the region of interest, note the following:

| | | |
|-----------------------|-------------|--|
| 1690 cm^{-1} | (ν_3) | $\nu(\text{C}=\text{O})$ |
| 1636 | (ν_4) | $\nu(\text{C}=\text{C}) + \delta(\text{OH})$ |
| 1448 | (ν_5) | $\delta(\text{O}-\text{H}\dots\text{O})$ |
| 1448 | (ν_1) | $\nu(\text{C}-\text{O})$ |
| 1320 | (?) | not assigned |

We recorded the ac absorption spectrum (with the laser beam chopped). These intensities must be corrected for the contribution from fluorescence (see Fig. 3). The peaks and valleys in the ac spectrum were assigned either to new species, where there was an increase in the absorption, or to a loss of the parent species where there was a decrease in absorption. Then, at selected frequencies (i.e. either at maxima or minima in the ac spectrum) we determined the time dependence of the transmitted intensity. To optimize the low S/N ratio for the recorded ac spectra, and the time profiles at the selected frequencies, the detected signal was scanned repeatedly and digitized with the infrared beam on, and blocked (TMC CAT Model 400). Such difference spectra were obtained for several low pressures of the hexafluoro-acetylacetone (1-4 Torr) to which small amounts of SF_6 were added (0.2-0.4 Torr) to serve as a heat transfer agent.

The T-jump induces a decrease in population at approximately 1650 cm^{-1} (ν_4), the parent species. This band shows a significant delay in attaining its maximum: $\tau_{\text{chem}} \approx 2 \text{ ms}$, compared

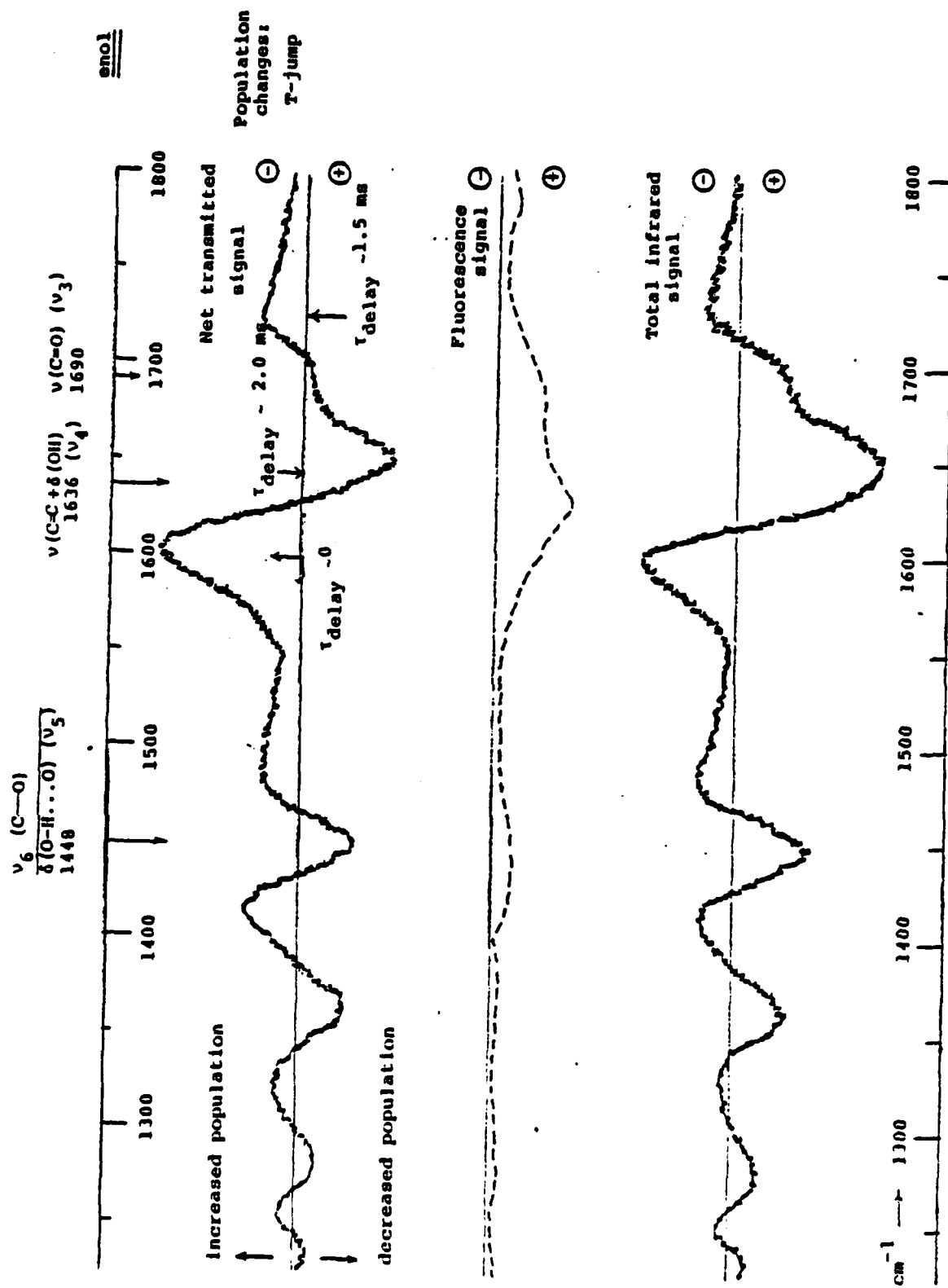


FIGURE 3. ac Spectra

with the laser heating pulse of ≈ 1 ms. An increase in population is indicated at 1602 cm^{-1} . This is a new band, located on the shoulder of ν_4 . Since it shows no time shift in attaining its maximum, we must ascribe it to absorption by a rapidly generated transient. There is a small increase in absorption, that is, an increase in population, characterized by a band at 1724 cm^{-1} . This band shows a small but definite delay beyond the maximum fluorescence intensity. It is quite close to ν_3 and we presume that their wings overlap. We interpret this band to be due to the keto form, such that the loss in population indicated by ν_3 of the enol partially detracts from the full increase in the absorption band due to production of the keto form.

A complete kinetic model has now been developed. Define the instantaneous concentration of the enol by

$$[\text{en}] = [\text{en}]_0 (1 - \gamma_0) - \phi(t)$$

where $[\text{en}]_0$ denotes the total amount of AcAc present

γ_0 denoted the fraction of the total in enol form,
at T_0

$\phi(t)$ denotes the loss in enol due to the temperature
pulse.

Then,

$$\phi(t) = \exp\left(-\int_0^t A \, dt'\right) * \int_0^t B \exp\left(+\int_0^{t''} A \, dt''\right) dt'$$

where

$$A(t') = k_f[M] \{1 + 1/K_{eq}\}$$

$$B(t') = k_f[M] \{1 - K_0/K_{eq}\} \left[\frac{\gamma_0[\text{en}]_0}{K_0}\right]$$

Since both k_f and K_{eq} are $T(t')$ dependent, solution for $\phi(t)$ was obtained via a computer program written for a bimolecular reaction wherein the temperature follows the shape indicated by the fluorescence pulse. Then we search for the best match of the recorded $\phi(t)$ curves with those computed for a range of parameters.

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